# Process Technology for Tunable Fischer Tropsch Synthesis Towards Middle Distillate Fuel Fractions

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14. ABSTRACT
**Develop Fischer Tropsch technologies that target the production of TP SBF through process, catalyst, and reactor improvements. Investigate Supercritical Fischer Tropsch Synthesis (SC-FTS) process performance as related to key reaction conditions. Develop Fe catalysts that operate over a wider range of process conditions in Supercritical Fischer Tropsch Synthesis (SC-FTS). Intergrate Iron-based SC-FTS into multiple bed reactor system that incorporates oligomerization and cracking/isomerization to improve desire product selectivity and quality.**

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# Objectives

– Develop Fischer Tropsch technologies that target the production of FT SBF through process, catalyst, and reactor improvements.

– Investigate Supercritical Fischer Tropsch Synthesis (SC-FTS) process performance as related to key reaction conditions.

– Develop Fe catalysts that operate over a wider range of process conditions in Supercritical Fischer Tropsch Synthesis (SC-FTS)

– Integrate Iron-based SC-FTS into multiple bed reactor system that incorporates oligomerization and cracking/isomerization to improve desired product selectivity and quality

# Iron – v – Cobalt

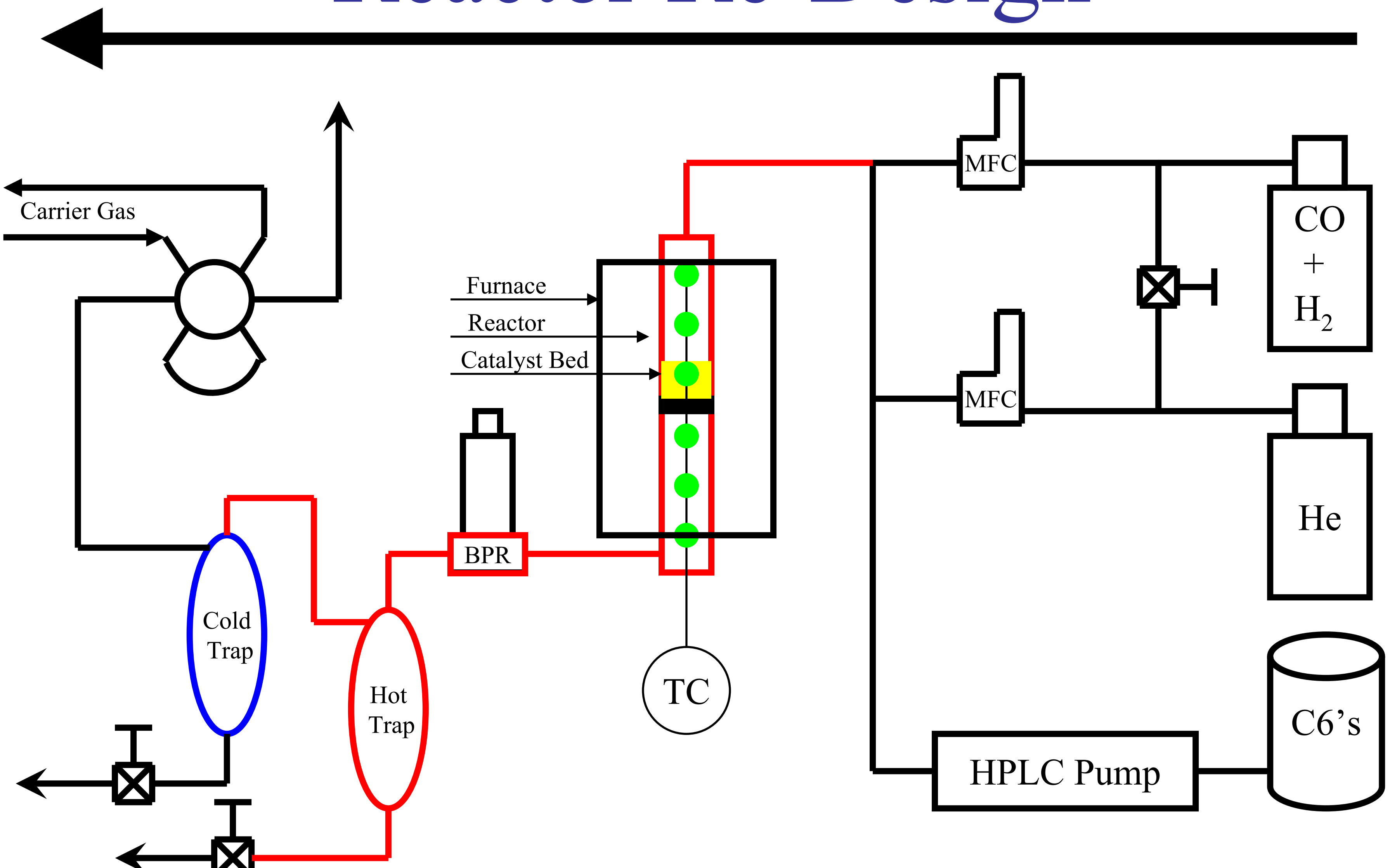
- Iron is less active and less expensive than cobalt

- Iron gives less methane, more olefins, and comparable maximum propagation probability

- Water Gas Shift (WGS) activity and the differing mechanism result in a lower $H_2$:CO usage ratio, allowing for a lower $H_2$:CO syngas ratio.

R. L. Espinoza, A. P. Steynberg, B. Jager, A. C. Vosloo**:** *Low temperature Fischer–Tropsch Synthesis from a Sasol Perspective*. **Applied Catalysis A: General** (1999): V 186, I 1-2, p13.

# Reactor Re-Design



# Reactor Re-Design

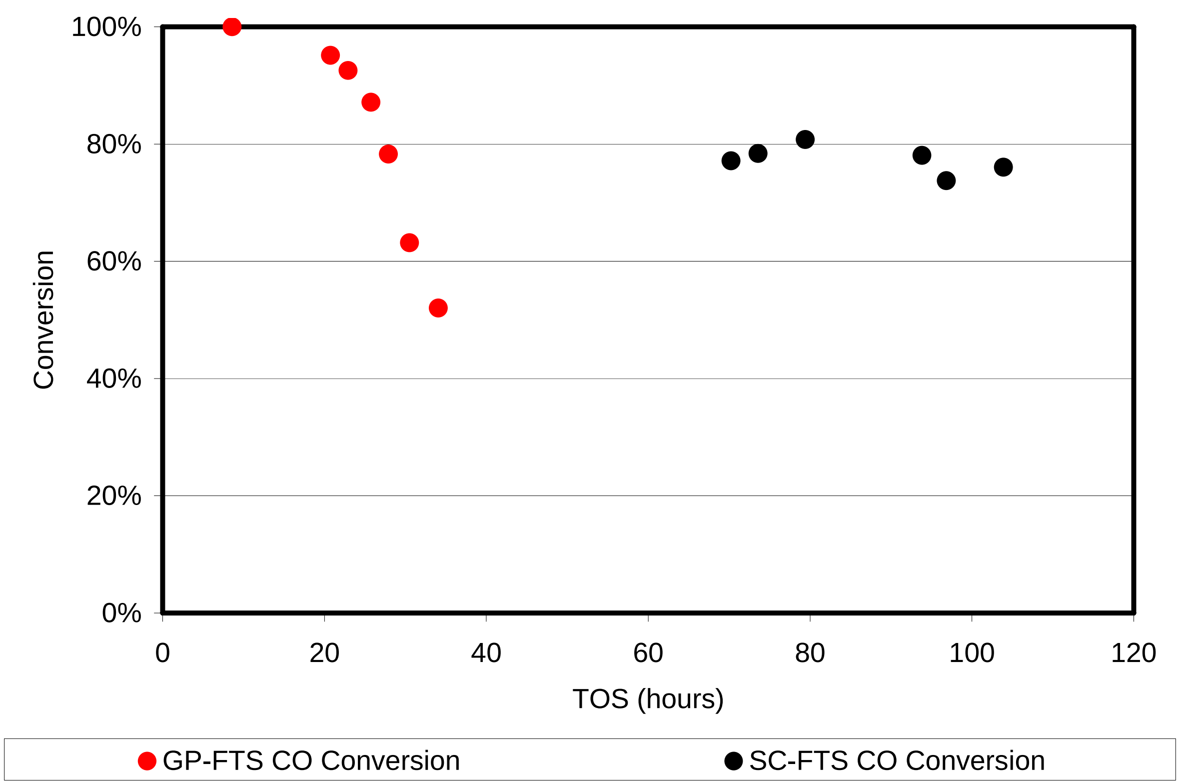
# Cobalt Fischer Tropsch

## Gas Phase –v– Supercritical (SC) Phase FTS

- 1.5 g of 20% Co / $Al_2O_3$
- Catalyst reduced in situ for 4 hours in 50 SCCM hydrogen at $T = 400^oC$ and $P \approx 3$ bar
- During gas phase FTS operation, pressure was maintained at 15 bar. During supercritical operation, the pressure was maintained at 65 bar (15 bar syngas partial pressure). Reaction temperature maintained at $240^oC$.
- Syngas: 2% $N_2$ (internal standard), 31% CO, 67% $H_2$ (Syngas Ratio = 2.15)

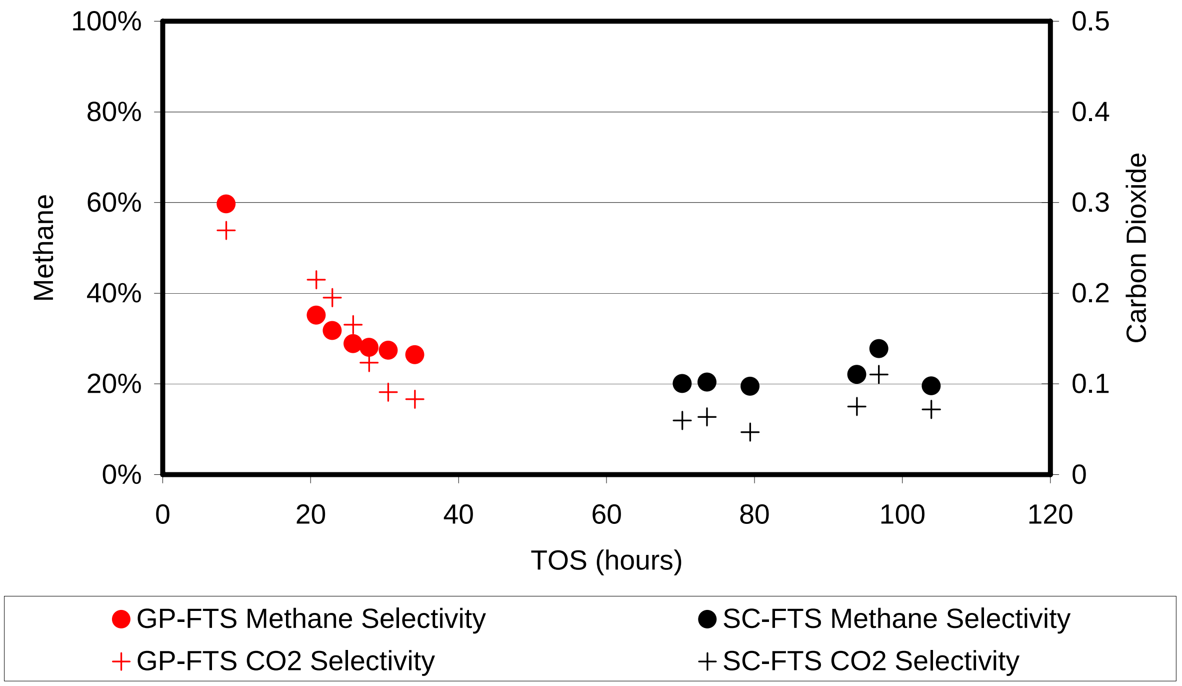
# Cobalt Fischer Tropsch

## Gas Phase –v– SC Phase: Conversion



# Cobalt Fischer Tropsch

## Gas Phase –v– SC Phase: Gas Selectivities

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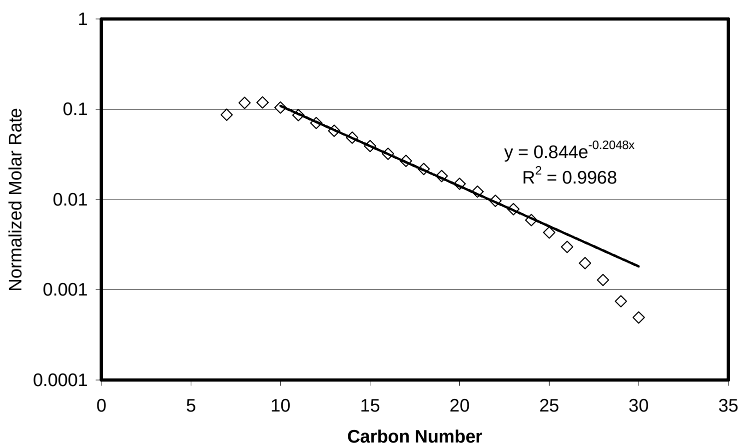
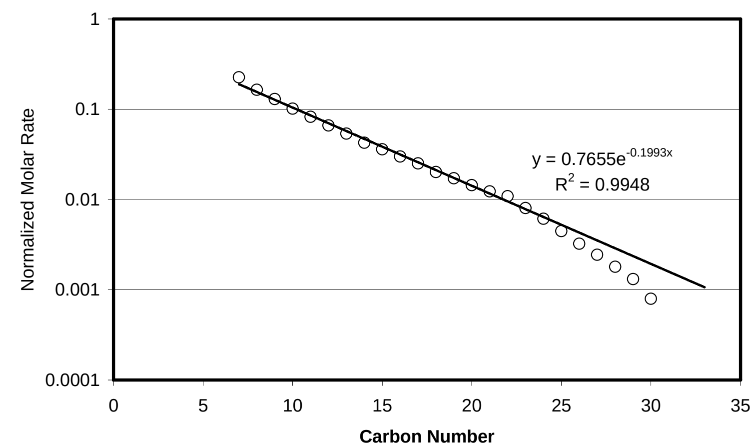
# Cobalt Fischer Tropsch

## Gas Phase –v– SC: Liquid Product Distribution

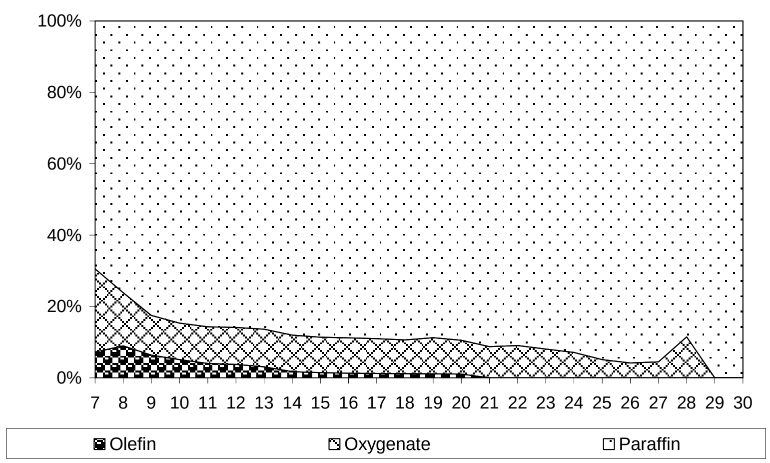
**GP-FTS ASF Plot (Propagation Probability = 80%)**



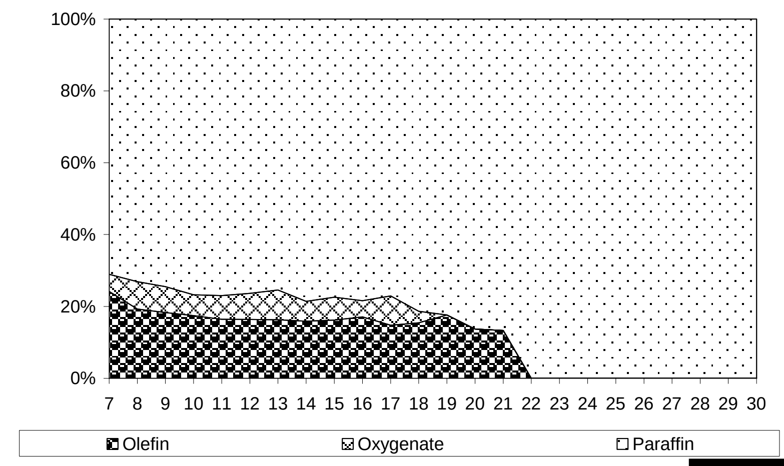

**SC-FTS ASF Plot (Propagation Probability = 80%)**




**GP-FTS Product Type**




**SC-FTS Product Type**

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# Summary from Cobalt Studies

- Redesigned reactor matches previous performance for both GP-FTS and SC-FTS.
  - Lower Methane and CO2 selectivity in SC-FTS.
  - Improved olefin selectivity in mid range products in SC-FTS.
  - Comparable catalyst activity with GP-FTS and SC-FTS.

# Iron Catalyst Preparation (I)

Iron Solution

→ 1.0 M iron nitrate hydrate (Sigma Aldrich 216828),

→ 0.11 M Zinc Nitrate Hydrate (SA 228737)

Reducing Solution

→ Saturate Ammonium Carbonate (SA 207861)

Potassium Precursor

→ Potassium Carbonate (SA 209619)

Copper Precursor

→ Copper Nitrate Hydrate (SA 223395)

Senzi Li, Sundaram Krishnamoorthy, Anwu Li, George D. Meitzner, Enrique Iglesia: *Promoted Iron-Based Catalysts for the Fischer–Tropsch Synthesis: Design, Synthesis, Site Densities, and Catalytic Properties*. **Journal of Catalysis** (2002): V 206, I 2, p202.

# Iron Catalyst Preparation (II)

- 2 mL / minute of Iron Solution added to 100 mL DIUF Water maintained at 80°C (Reducing Solution added manually to maintain pH at 7) until solution volume reaches 250 mL.
- Slurry Filtered. Solid redispersed in DIUF and filtered 3 times.
- Catalyst redispersed in drying liquid (DIUF water or ethanol) then filtered.
- Filter Cake dried overnight at 80oC then calcined for 1 hour at 350°C

# Iron Catalyst Preparation (III)

- Incipient Wetness Used to impregnate Potassium Solution onto Iron (K / Fe atomic ratio = .02). Catalyst dried overnight at T = 80$^{o}$C then calcined for 1 hour at T = 350$^{o}$C
- Incipient Wetness Used to impregnate Copper Solution onto Iron (Cu / Fe atomic ratio = .01). Catalyst dried overnight at T = 80$^{o}$C then calcined for 1 hour at T = 350$^{o}$C
- Filter Cake dried overnight at 80$^{o}$C then calcined for 1 hour at 350$^{o}$C
- Catalyst reduced in situ with syngas at T = 270$^{o}$C, P = 4.5 bar.

# Pore Volume of Pre-Promoted Iron Catalyst

- Saturated with DIUF water prior to drying

  → Pore Volume ≈ 0.2 mL / g

- Saturated with ethanol prior to drying

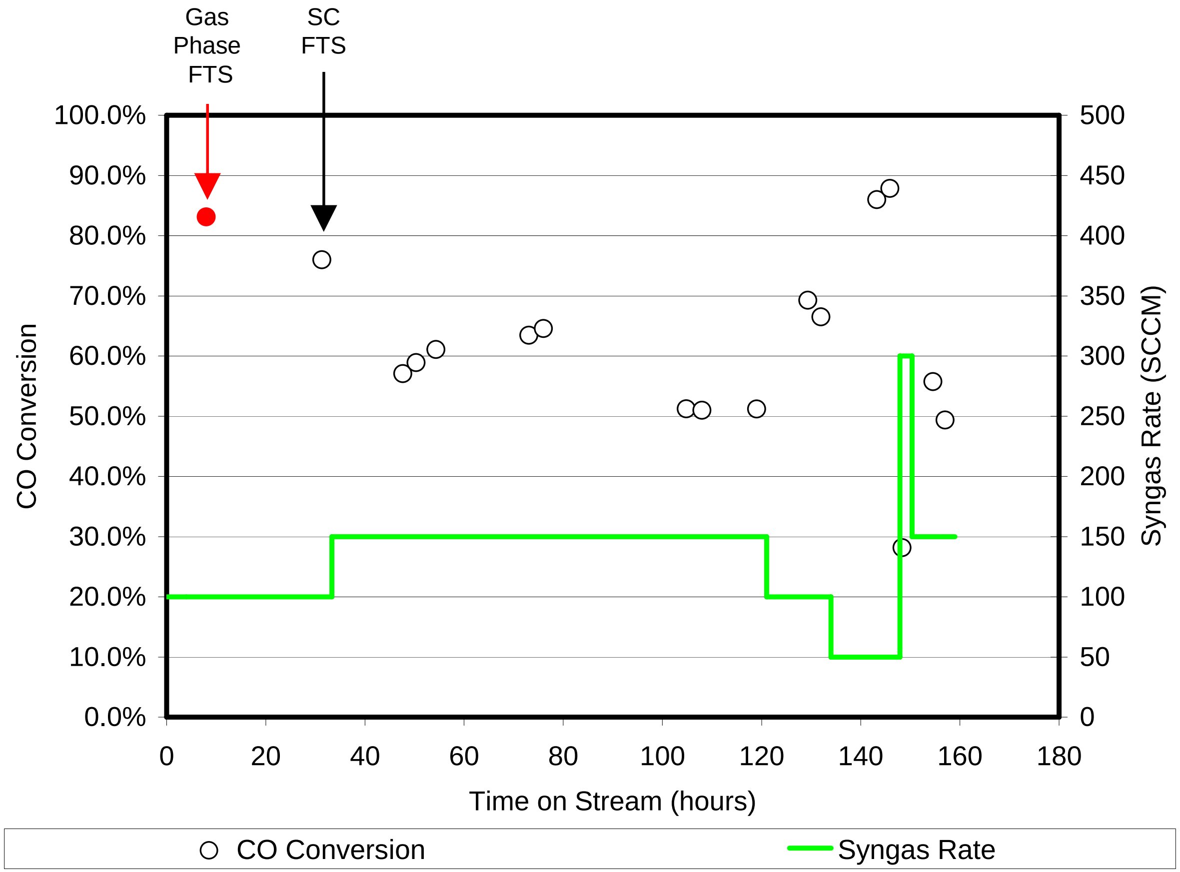
  → Pore Volume ≈ 1.0 mL / g

# Fischer Tropsch Parameters

- 2 g of calcined promoted catalyst loaded into reactor
- Syngas is 1.5% $N_2$, 37.1% CO, 61.4% $H_2$ (Syngas Ratio = 1.65)
- During supercritical operation, the ratio of hexanes to syngas feed is 1 mL / 50 SmL
- 21 bar pressure during GP-FTS, 75 bar pressure during SC-FTS (17 bar syngas partial pressure).
- T = 240$^o$C for most of study

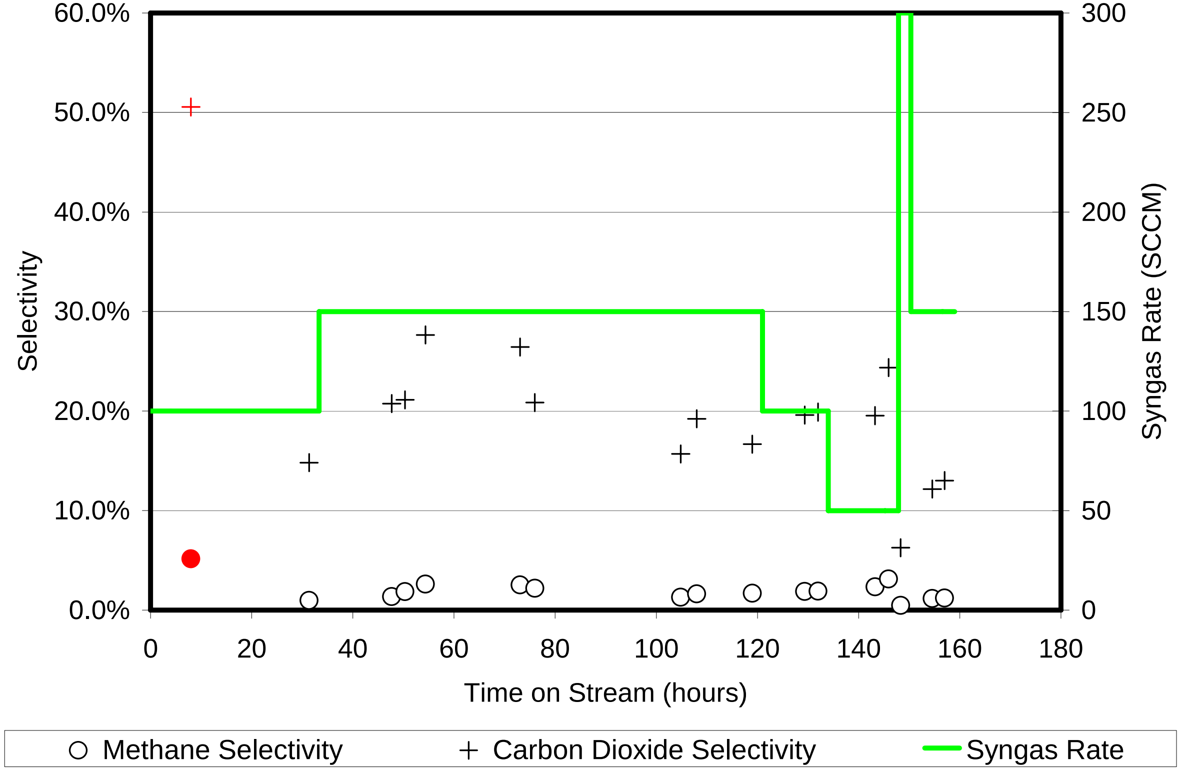
# Iron SC-FTS Performance

## Conversion



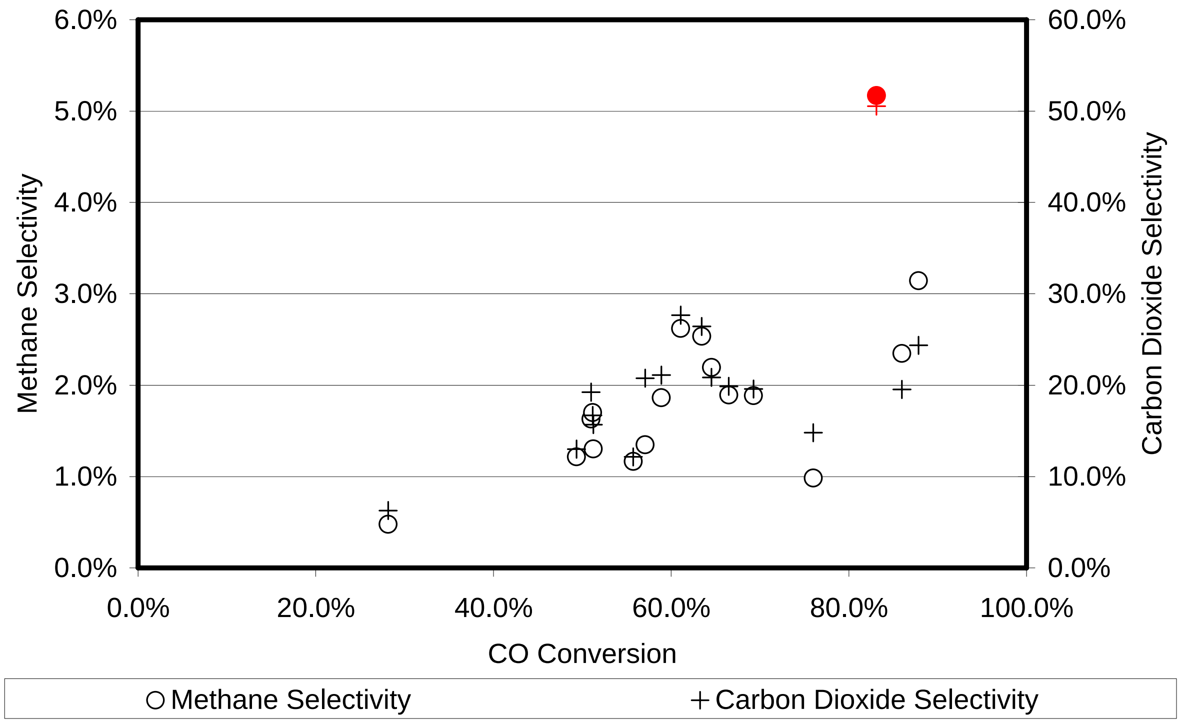
# Iron SC-FTS Performance

## Methane and $CO_2$ Selectivity



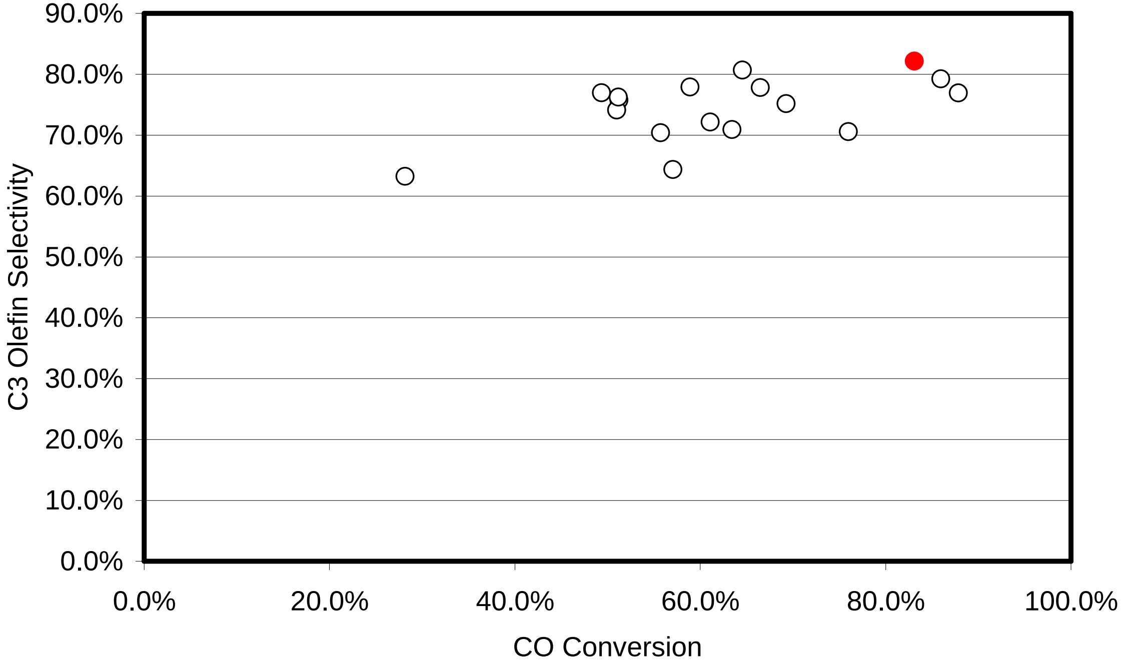
# Iron SC-FTS Performance

## Selectivity Cross-Plot

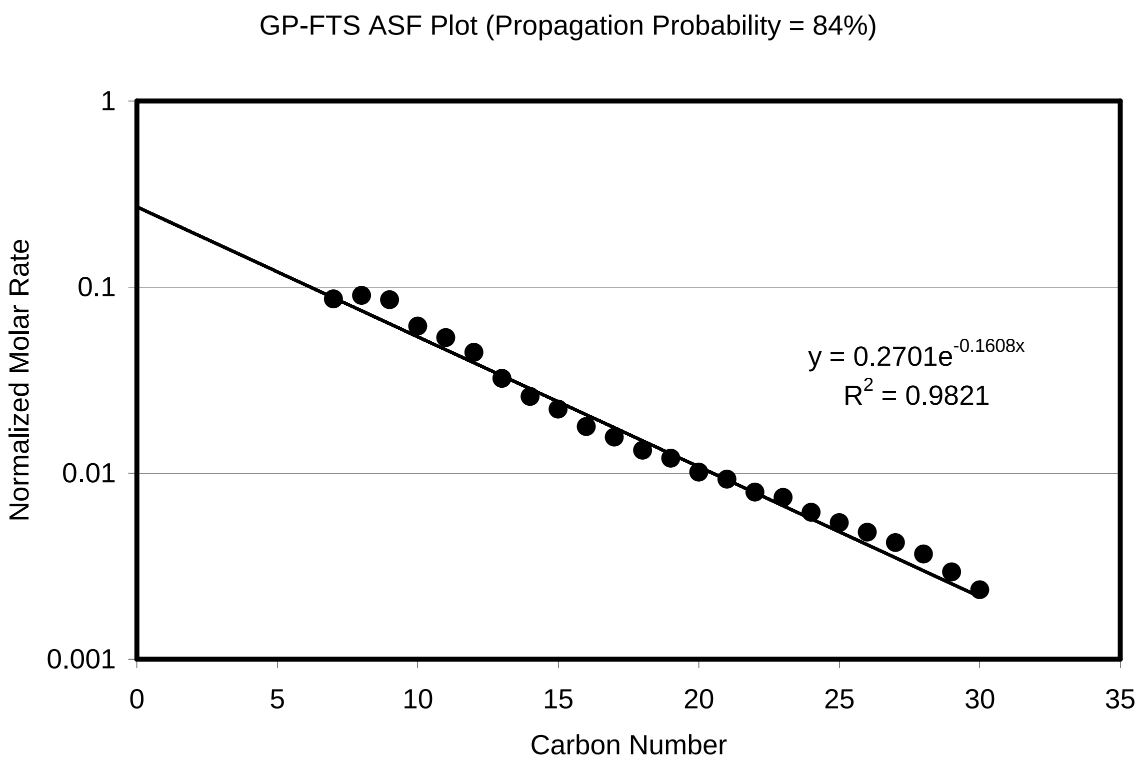


# Iron SC-FTS Performance

## C3 Olefin Selectivity Cross-Plot



# Iron GP-FTS Performance
## Liquid Products: ASF Plot

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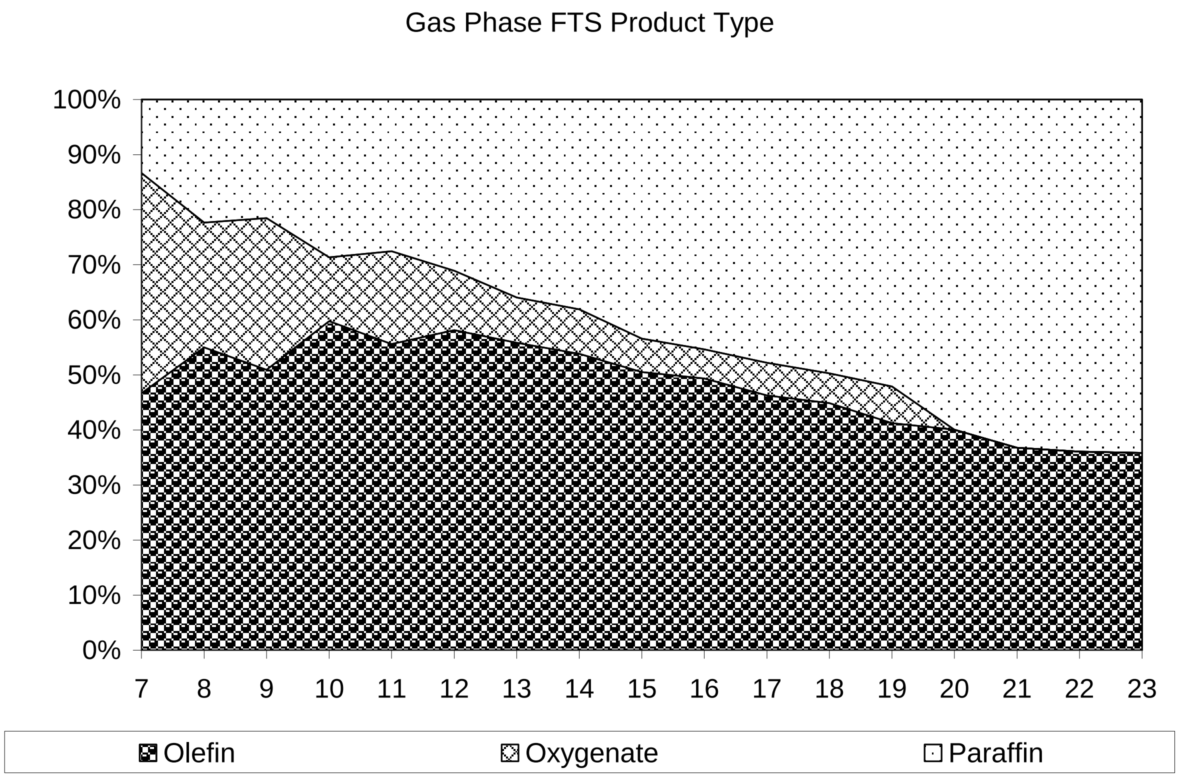
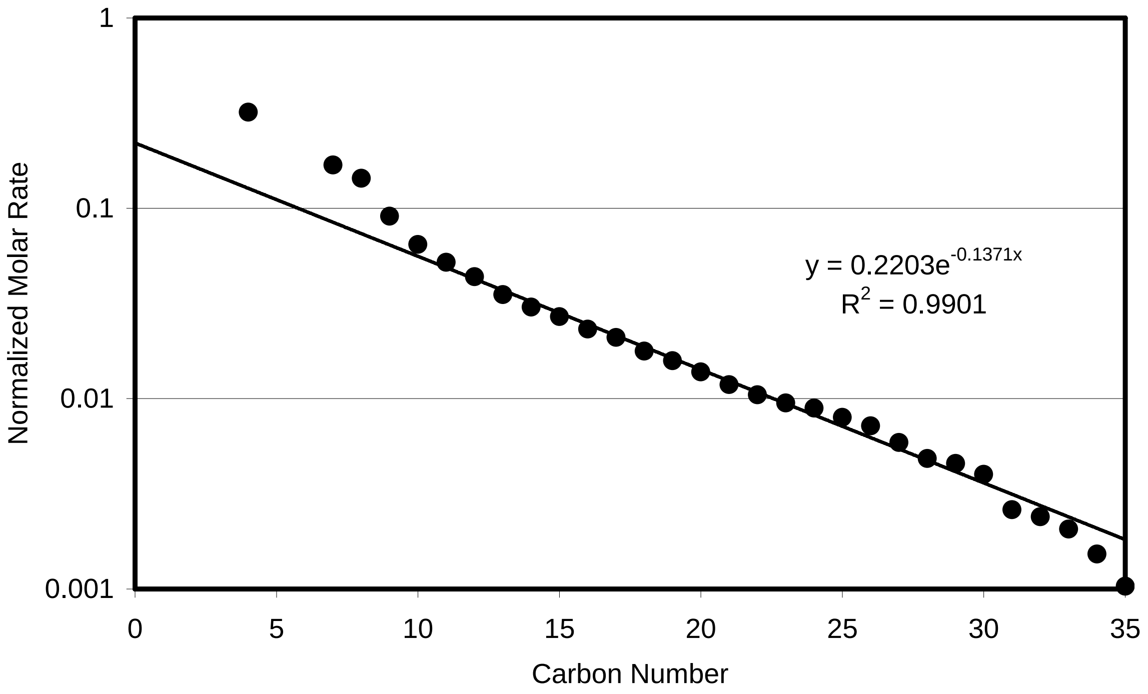
# Iron GP-FTS Performance

## Liquid Products: Product Type



# Iron SC-FTS Performance
## Liquid Products: ASF Plot

SC-FTS ASF Plot (Propagation Probability = 86%)

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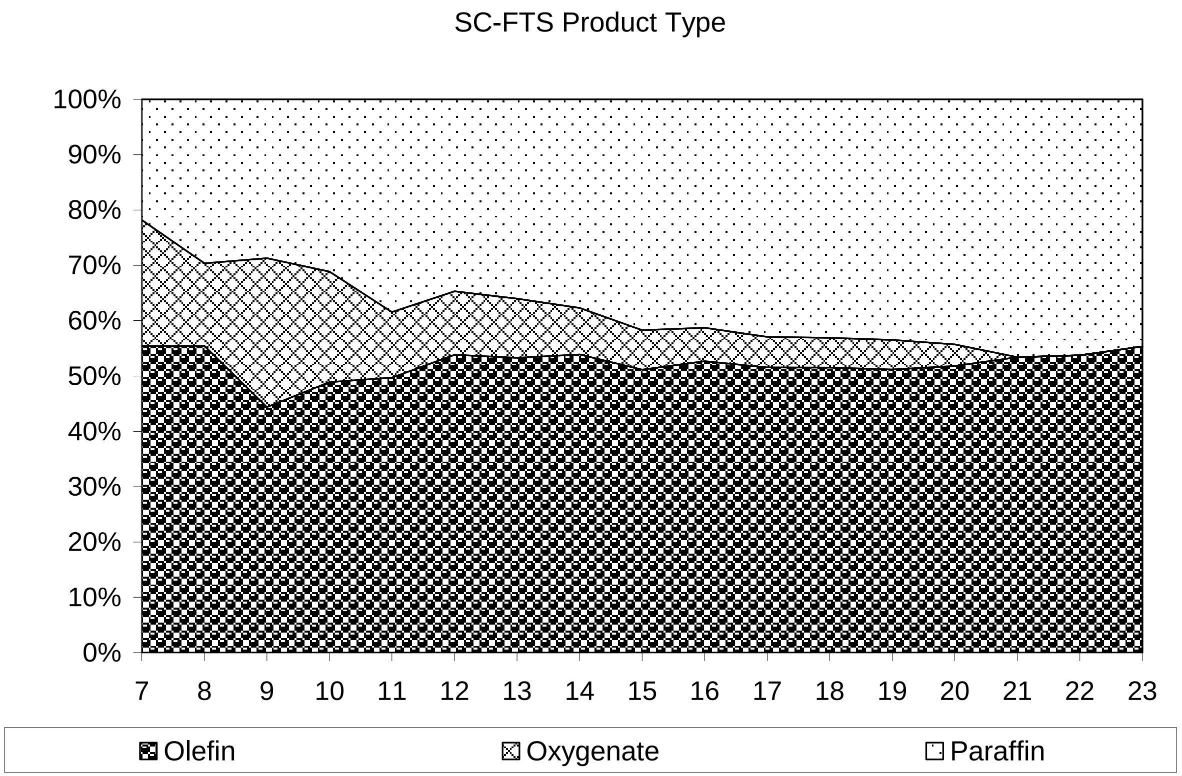
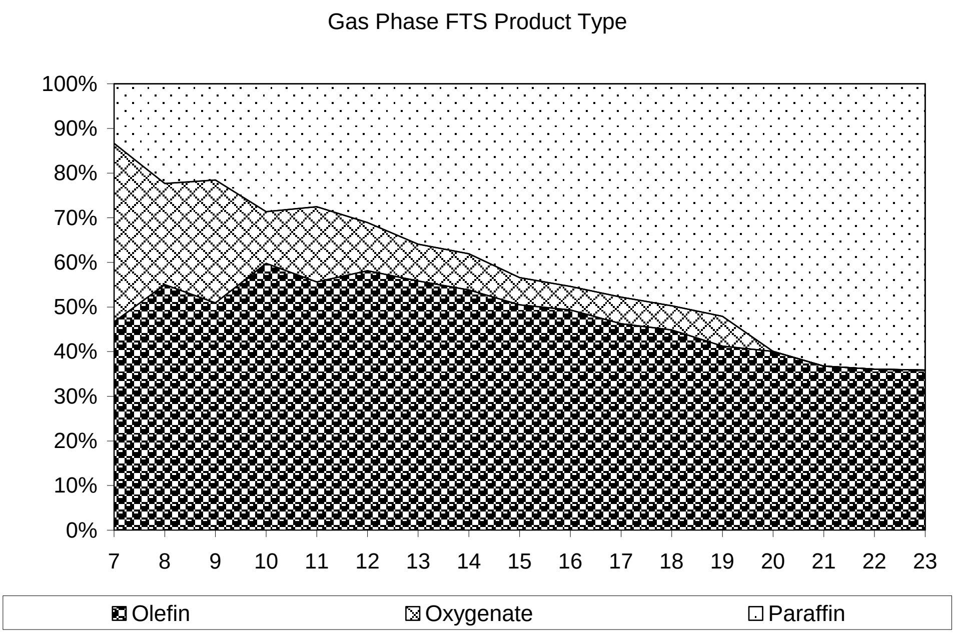
# Iron SC-FTS Performance

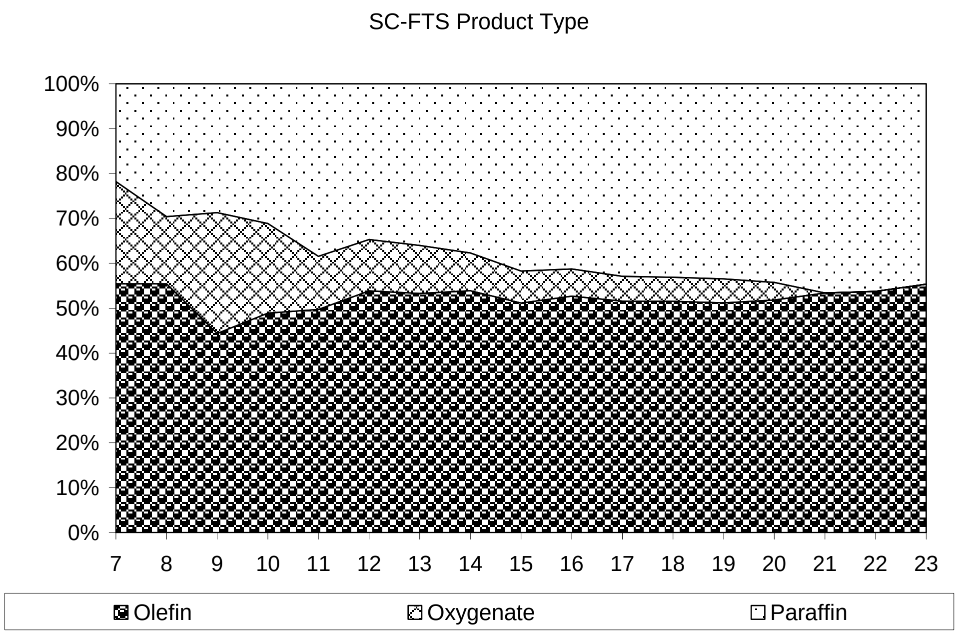
## Liquid Products: Product Type



# FTS Product Type Comparison

## GP-FTS –v- SC- FTS on Iron Catalyst




- SC-FTS maintains the olefin selectivity in the middle and wax fractions better than GP-FTS.

# Conclusions

- We have successfully synthesized an effective iron Low Temperature Fischer Tropsch (LTFT) catalyst and tested it under both gas phase and supercritical phase conditions.

- The iron catalyst demonstated much higher olefin selectivity, chain growth probability, and $CO_2$ selectivity than we have observed on cobalt while yielding a lower methane selectivity.

- The benefits of SC-FTS realized with a cobalt catalyst (decreased methane and CO2 selectivity and enhanced middle and heavy olefin selectivity) were also achieved on this iron catalyst.

# Future Work

- Compare Gas Phase and Supercritical Phase for Iron LTFT Operation
- Study the influence of basic process parameters (temperature, pressure, etc.) on process performance.
- Compare traditional Iron FT catalyst with composite nanoparticles on a porous and non-porous support.
- Integrate Iron-Based FT into 3-Bed Reactor that incorporates oligomerization and cracking/isomerization to improve desired product selectivity and quality.

# Acknowledgements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# Questions